Intercomparison of Stable Isotope Measurements of CO_2

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INTRODUCTION

Over the last decade the two most extensive, high-precision measurement programs measuring the $\delta^{13}C$ of CO_2 [*Keeling et al*, 1989; *Whorf et al.*, 1993; *Francey et al.*, 1990] have resulted in data that have very different implications for the global carbon budget over the period [*Francey et al.*, 1995a]. The $\delta^{13}C$ data are primarily used to partition the uptake of fossil carbon emissions between ocean and terrestrial plant reservoirs. The requirement for high precision in these measurements was emphasized by *Enting et al.* [1993, 1994] and *Tans et al.* [1993] and the requirement for extensive spatial coverage by *Ciais et al.* [1994]. The recent advent of isotopic measurements on the extensive CMDL flask network has added stimulus for a number of improvements in the intercalibration of isotope measurement programs. This report gives preliminary results from one such program where a subset of CMDL flasks filled at Cape Grim, Tasmania, were analyzed with both CSIRO and INSTAAR mass spectrometer facilities. The results were compared to the long running CSIRO in situ CO_2 extraction program at Cape Grim [*Francey et al.*, 1995b].

The normal mass spectrometric measurement of $\delta^{13}C$ in atmospheric CO_2 requires the simultaneous measurement of ion currents because of three mass-to-charge ratios (m/e) at 44, 45, and 46. The m/e 46 is primarily measured so that any ^{17}O contribution to the m/e 45 can be calculated and removed in order to obtain the actual ^{13}C contribution. With some precautions, a bonus is a record of the $\delta^{18}O$ in atmospheric CO_2, a useful tracer in its own right. An explanation that described the global distribution of this species was first presented by *Tans et al.* [1986] and *Francey and Tans* [1987], and subsequently further expounded by *Farquhar et al.* [1993]. An intercomparison of the measurements of $\delta^{18}O$ in CO_2 shows considerable systematic influence, but the preliminary data are included for completeness.

METHODS

The isotopic analysis of air collected in CMDL flasks filled at Cape Grim commenced in December 1991 and still continues; data are presented for samples collected to the end of 1993. The 2.5-L glass flasks are flushed for 5 minutes at 8 L min^{-1}, then pressurized to around 0.4 bar above ambient. The air is sealed using Teflon O-ring valves. For details of the sample collection procedure for flasks in the CMDL-INSTAAR network see *Conway et al.* [1994] and associated references.

A subset of the flasks (Table 1) is routed through the CSIRO/DAR Global Atmospheric Sampling Laboratory (GASLAB) in Aspendale, where about 150 bar-mL of air is used for the duplicate determinations of CO_2, CH_4, CO, H_2, and N_2O by gas chromatography. Comparisons of results from Aspendale and Boulder for these species will be the subject of a separate report (*Steele et al.,* in preparation, 1994). An additional 30-50 bar-mL of the flask air provides $\delta^{13}CO_2$ and $\delta^{18}CO_2$ using a Finnigan MAT 252 mass spectrometer with MT Box-C accessory for the extraction of CO_2 from the air.

Flasks are then returned to Boulder, Colorado, for analysis by CMDL and INSTAAR. The CMDL Carbon Cycle Division analyzes the air for the mixing ratio of CO_2 using a non-dispersive infrared analyzer and for mixing ratios of CH_4, CO, and H_2 by gas chromatography [*Conway et al.*, 1994, *Steele et al.*, 1987, *Novelli et al.*, 1992]. The Stable Isotope Laboratory at INSTAAR uses ~700 bar-mL of the sample to determine the $\delta^{13}C$ and $\delta^{18}O$ of the CO_2 using a Vacuum Generators SIRA Series II mass spectrometer that is equipped with a "triple-trap" assembly to cryogenically separate CO_2 from the air sample (*M. Trolier et al.*, Monitoring the stable isotopic composition of atmospheric CO_2: measurements from the CMDL global network, in preparation, 1995).

Calibration strategies for the mass spectrometer raw data and correction strategies for the isotopic

TABLE 1. Annual Average and Standard Deviation of $\delta^{13}C$ for the Cape Grim In Situ Method and for Corrected GASLAB and INSTAAR Measurements

$\delta^{13}C$	In situ	GASLAB	INSTAAR
1992	-7.756	-7.759	-7.752
(n = 2)	(0.031)	(0.028)	(0.038)
1993	-7.759	-7.758	-7.765
(n = 44)	(0.030)	(0.029)	(0.044)

determinations are critical considerations. This reflects the fact that the scientific requirement is for an inter-laboratory precision in average $\delta^{13}C$ values close to, or better than, the instrument internal precision on an individual analysis. In this intercomparison it was found necessary to consider the following factors: (a) the assumed isotopic composition of the primary international reference materials, (b) the methodology used to determine the isotopic composition of secondary or working standards, (c) the algorithms employed to calculate the ^{13}C and ^{17}O contributions to the m/e 45 ion beam intensity (the ^{17}O correction), (d) the constants and trace gas concentration calibration scales used in the estimation of the N_2O contribution to the m/e 44 ion beam current, (e) modification of the isotopic composition of the working standard CO_2, (f) isotopic fractionation in the extraction of CO_2 from whole air samples, and (g) mixing of sample and working standard CO_2 in the mass spectrometer ion-source region.

Points (a), (b), and (c) have recently been addressed in detail [*Allison et al.* 1994a,b, *Allison and Francey,* 1994]. Summarizing, both the CSIRO and INSTAAR mass spectrometer values were corrected using the same recommended values for the isotopic composition in the hypothetical V-PDB international isotope standard, and both laboratories have related the measured δ^{45}, and δ^{46} of samples to the primary standard by the measured δ^{45}, and δ^{46} of intermediate standards to avoid propagation of errors associated with the ion corrections. The same assumption about the relationship between ^{17}O and ^{18}O [*Craig*, 1957] is then applied in the conversion of the final ratios to $\delta^{13}C$, $\delta^{18}O$.

Point (d) uses a correction involving the ratio of N_2O/CO_2 in the sample and a relative ionization efficiency of the two gases in the mass spectrometer source [*Mook et al.*, 1983]. At DAR a relative ionization efficiency of 0.72 ± 0.01 has been measured (C.E. Allison, private communication, 1994). The CO_2 concentrations used to determine the N_2O/CO_2 ratio in the sample are the GASLAB measured values for the flask, calibrated against a suite of standards, linked in 1993 to the CMDL scale to better than 0.1 ppmv. For N_2O a nominal 310 ppbv was employed; the annual average value at Cape Grim in 1992 is estimated at 310 ppbv [*Montzka et al.*, 1993]. At INSTAAR, the relative ionization efficiency of N_2O/CO_2 has been measured at 0.754 ± 0.010 on the SIRA Series II instrument [*Gemery*, 1993]. The CO_2 mixing ratios used in the N_2O correction for each flask are the values measured by CMDL on the same flasks. The N_2O mixing ratios are approximated from global mean values determined at CMDL, taking the global mean for January 1, 1993, to be 310 ppbv, with a linear growth rate of about 0.66 ppbv yr^{-1} [*Montzka et al.*, 1992].

A typical N_2O correction to $\delta^{13}C$ is -0.2‰, and an error of 1% in N_2O or CO_2 concentration results in a $\delta^{13}C$ error of <0.003‰, considered negligible in the present case. There are potential differences because of

errors in the determination of the relative N_2O/CO_2 ionization efficiency, but they are relatively small. For example, a +5% error translates into changes of -0.006‰ and -0.009‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

Point (e), the modification of standard CO_2 during analysis, refers to a fractionation of the CO_2 gas in the standard reservoir during bleed through the capillaries or waste line. At GASLAB a fractionation of about 0.0028‰ per hour in $\delta^{13}C$ of CO_2 in the standard reservoir is measured; the effect is twice as large for $\delta^{18}O$. This is documented by *Allison et al.* [1994a] for the MAT252 and a correction automatically applied to the data; in practice the standard reservoir is automatically refilled every four to six samples. For the MAT252 analysis of the CMDL flask data set, the average "bleed" correction amounted to 0.011 ± 0.009‰ in $\delta^{13}C$ and 0.023 ± 0.018‰ in $\delta^{18}O$, corresponding to a mean bleed time of 3.9 hours. The correction is made implicitly at INSTAAR by measuring a working standard (whole air) at the beginning and end of every analysis run, and linearly interpolating to account for all instrument drifts. The observed drifts are variable but are typically less than 0.05‰ for $\delta^{13}C$ (over 8 hours); they are probably dominated by instabilities in the VG SIRA mass spectrometer.

Point (f) addresses potentially significant differences arising from the different CO_2 extraction methods. The GASLAB MAT252 MT Box-C was supplied with a capillary to drop the sample pressure for cryogenic drying and CO_2 extraction in cold traps. In a typical flask analysis, about 30 bar-mL of air is bled through the capillary and two -180°C cold traps in series. The trap pressure rises from 0 to around 200 mb during this process in which the H_2O, CO_2, and N_2O are retained in the traps and the remaining air components are pumped away. In a succession of distillations, H_2O is then retained at -100°C and the mobile CO_2 and N_2O finally collected in a third cold trap at -180°C; maximum pressure in these transactions (the yield) is a few mb and about 0.5 µmol of CO_2 is collected. From here the sample CO_2 (and N_2O) is fed to the mass spectrometer changeover valve for analysis. The cryogenic separation scheme at INSTAAR is rather different. Because of the larger volume of air required for analysis, and the consequent drop in backing pressure within the sample flask, a mass flow controller is used instead of a capillary to limit the flow through the extraction system. The air is drawn through a high capacity glass trap held at -90°C to remove water (common to all samples), then through a stainless-steel trap at -196°C to remove CO_2 (N_2O). A flow rate of 60 bar-ml min^{-1} is used; the pressure in the traps during this process is typically a few mb. The yield of CO_2, about 12 µmol, is released to the mass spectrometer by expansion after warming the CO_2 trap.

On April 28, 1993, the GASLAB MT Box-C was modified to permit the analysis of very small (ice core) samples and operating parameters optimized for the

small sample analyses. The influence of the modifications on the routine measurements of flask samples is discussed below. The results from both the INSTAAR and GASLAB trapping boxes are compared to an independent manual system operated at Cape Grim as part of the long running in situ program [*Francey et al.*, 1995]. This system uses an air flow of 300 mL per minute over 2 hours, with trapping at a maximum pressure of 20 mb. The collected CO_2 is stored in 50 mL glass bulbs with a Teflon O-ring tap for analysis at Aspendale on the MAT252 mass spectrometer through the normal inlet variable volume.

Finally, point (g) brings up the potential for systematic errors arising from the mixing of sample and standard gases in the source region of the mass spectrometer. Similar effects were discussed by *Mook and Grootes* [1973] and were documented in the MAT252 (C. Flehoc et al., Systematic influences in the high precision stable isotope measurements of atmospheric trace gases, in preparation, 1995). They are emphasized by having a standard CO_2 with isotopic ratio very different from the sample CO_2 or by insufficient evacuation of the source region during normal sample-standard switching. The effect can be manifested as a sample size dependence in δ, but more importantly, a sample value biased towards the working standard isotopic ratio.

CALIBRATION STRATEGIES

Different calibration strategies are employed by the two groups. At GASLAB all isotopic values are routinely expressed relative to the one working-standard (high-pressure cylinder "HC453" CO_2) used in the reference reservoir of the MAT252. The working standard isotopic value is monitored each measurement session by prior calibration against an independent sub-sample of the working gas. The small difference of around 1‰ in $\delta^{13}C$ between ambient air and standard, minimizes possible sample-standard mixing effects. The calibration is also monitored by analysis of a high-pressure cylinder containing "standard" Cape Grim air, before, in the middle, and at the end of automatic sequences of sample analyses (typically 10 samples and 1 to 2 additional low pressure air standards). Generally, the air standard data has not been used to modify sample results, an exception being the so-called "APC correction" discussed below.

INSTAAR uses a different routine calibration strategy. INSTAAR's working standard is CO_2 in whole air, just as the samples are. The CO_2 gas in the mass spectrometer's standard reservoir is used only to relate samples to the working standard within the same analysis run, not as an isotopic reference material as is the routine at GASLAB. Several aliquots of the working standard are used at the beginning and end of each analysis run (typically 10-20 samples). The isotopic composition of the working standard is monitored monthly by intercalibration with other CO_2-in-air and pure CO_2 secondary standards.

RESULTS

The results of the intercomparison are shown in Figure 1(*a*) and (*b*) for $\delta^{13}C$ and $\delta^{18}O$, respectively. The main features of the $\delta^{13}C$ intercomparison are:

(a1) The flask record defines the seasonality of the in situ record faithfully in 1993 but not so well in 1992. This appears to be due to increased scatter in the early flask data.

(a2) The agreement between the annual mean levels of all three records is surprisingly good, particularly in view of the independent calibration of standards between the two laboratories. The annual averages and standard deviations for each year are summarized in Table 1. There is excellent agreement between the
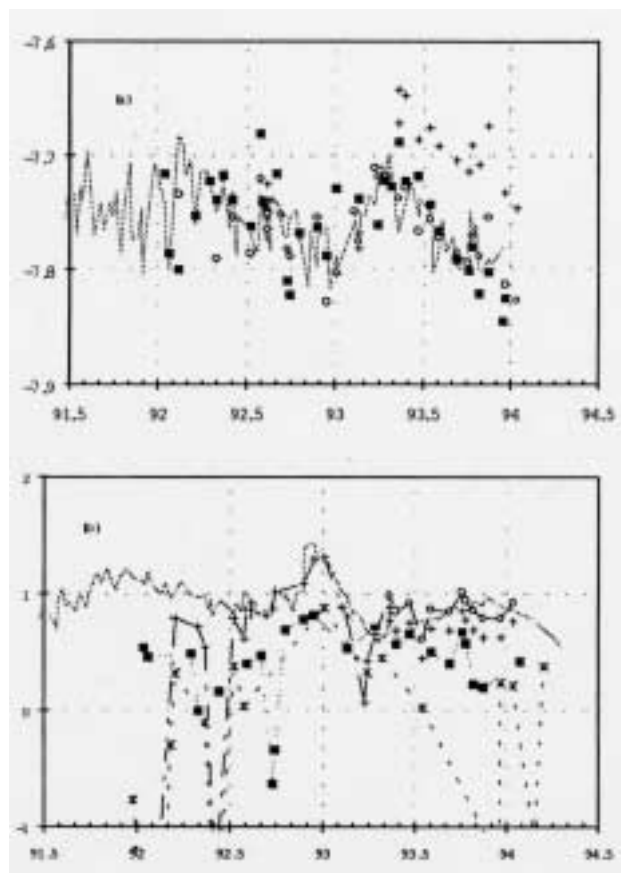

Fig. 1.   (*a*) The $\delta^{13}C$ of Cape Grim CO_2 measured in CMDL flasks by GASLAB (+: uncorrected, o: with "APC" correction) and INSTAAR (filled squares). The line connects measurements at GASLAB on CO_2 extracted in situ at Cape Grim. (*b*) The $\delta^{13}O$ of Cape Grim CO_2 measured in CMDL flasks. Symbols are as for $\delta^{13}C$, except that INSTAAR values are given separately for unflagged data (filled squares) and flagged data (stars). In this case the "APC/idle time" adjustment is not independently corrected, rather maintains the 1992 relationship with the in situ data (see text).

in situ and CMDL mean values. All values agree within one standard deviation (which include the seasonality). Taking only flasks analyzed on both GASLAB and INSTAAR instruments, the mean difference is negligible though this may be somewhat fortuitous as the scatter remains comparable to that in the annual averages.

$$\Delta\delta^{13}C(GASLAB-INSTAAR) = -0.004 \pm 0.034‰$$

(a3) The very good agreement in $\delta^{18}C$ is only achieved after all GASLAB analyses after April 28, 1993, are corrected by -0.081‰. At this time, the MT Box-C extraction line on the GASLAB MAT252 was modified to permit analysis of very small (ice core) air samples and operating parameters optimized. The capillary connecting the flask manifold to the cryogenic traps was by-passed (connected in parallel) with an "Automatic Pressure Flow Controller" (APC). Recent removal of the APC resulted in no change in calibration, and the step change in April 1993 is attributed to a change in mass spectrometer "idle time" which was increased from 12 to 20 seconds at that time (*C. Flehoc et al.,* Systematic influences in the high precision stable isotope measurements of atmospheric trace gases, in preparation, 1995). The correction of -0.081 ± 0.010‰ was obtained from least squares regressions to the data obtained from the most frequently analyzed of our air standards (ALVZ861) before and after the APC installation and idle time change, though slightly larger uncertainty is obtained by averaging the results from several other air standards in use around this time (C.E. Allison*, private communication, 1993).* The comparison here supports the magnitude of the standard-derived correction, and highlights the potential for significant differences in $\delta^{13}C$ to arise from apparently minor changes to routine.

For $\delta^{18}O$, the situation is less satisfactory. This reflects the fact that the CMDL flasks are filled without drying of the sample air and so are susceptible to oxygen exchange between CO_2 and trace water inside the flask. Isotopic composition of the trace water (i.e., past flask history) is likely to be an important influence [*Gemery,* 1993]. It also reflects the fact that the GASLAB APC correction is not yet well defined by independent analyses of GASLAB air standards. For $\delta^{18}C$, most air standards are relatively stable and extrapolation of results from several standards gives a consistent correction. This is not the case for $\delta^{18}O$ where drifts are a common feature in the GASLAB tanks, and in particular in the tank in most use around the time of the APC installation. The small sample size employed in GASLAB almost certainly emphasizes the difficulty.

In Figure 1*b* an "APC adjustment" was applied to the GASLAB measurements that maintains the relationship between the flask and in situ measurements and between the GASLAB and INSTAAR measurements on the flasks. This determines an effective $\delta^{18}O$ APC correction for use in further study of the effect at GASLAB. The main features of Figure 1*b* are:

(b1) Despite several outliers, the flask data record features of the in situ $\delta^{18}O$ record (in which the opportunity for oxygen exchange in flasks is considered negligible).

(b2) The INSTAAR values are, on average, significantly lower than the GASLAB numbers. Excluding INSTAAR values, and using only pre-APC GASLAB data, only 5 points are available, for which:

$$\Delta\delta^{18}O(GASLAB-INSTAAR) = -0.443 \pm 181‰.$$

Allison et al. [1994*a*] have postulated that a slowly (1-2 year) converging difference in $\delta^{18}O$ between the new MAT252 and previous VG602D at GASLAB, was a readjustment of the isotopic content of trace water in the MAT252 instrument from closer to northern continental (depleted) to closer to southern ocean ambient water values. The present results are qualitatively in this sense, as is the sense of the outliers. The mean $\delta^{18}O$ of precipitation at INSTAAR is about -8‰, very similar to the values for Germany and UK, from where the various mass spectrometers originate. At Cape Grim latitudes around -4‰ is observed [*Yurtsever and Gat*, 1981], and the assumption is that the VG602D, purchased in 1976, had equilibrated towards this value because of exposure to room air during maintenance, power failures, etc. The outliers, when appearing in the results from both laboratories, presumably reflect oxygen isotope exchange between CO_2 and trace water condensed within individual flasks [*Gemery*, 1993]. Outliers in INSTAAR data alone could reflect exchange occurring during shipment of the flasks to Boulder. (b3) There is reasonable agreement in the temporal behavior between the majority of GASLAB flask samples and the in situ samples, and similarly between the GASLAB and INSTAAR measurements on individual flasks. This suggests that many of the CMDL flasks, despite the potential for contamination by water, are reflecting atmospheric values at Cape Grim.

CONCLUSIONS

Considering the very preliminary state of intercalibration between the two laboratories, and the potential for systematic error in both the CO_2 extraction and mass spectrometric isotope ratio determination, there is excellent agreement in $\delta^{13}C$ measured on Cape Grim

samples. The merging of data sets used by *Ciais et al.* [1994] for inversion studies is strongly supported by the data presented here.

The confirmation of the large shift in the GASLAB flask $\delta^{13}C$ compared to the in situ record and the CMDL flask results, accompanying relatively minor plumbing modification of the trapping box inlet, emphasizes the potential for serious interlaboratory discrepancies. The importance of calibrations using whole air standards, and redundancy in measurement and calibration strategies is obvious.

It is also clear that much more work is required to achieve similar consistency and compatibility in the measurements of $\delta^{18}O$ in CO_2, though there are quite encouraging sections of the intercomparison record.

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